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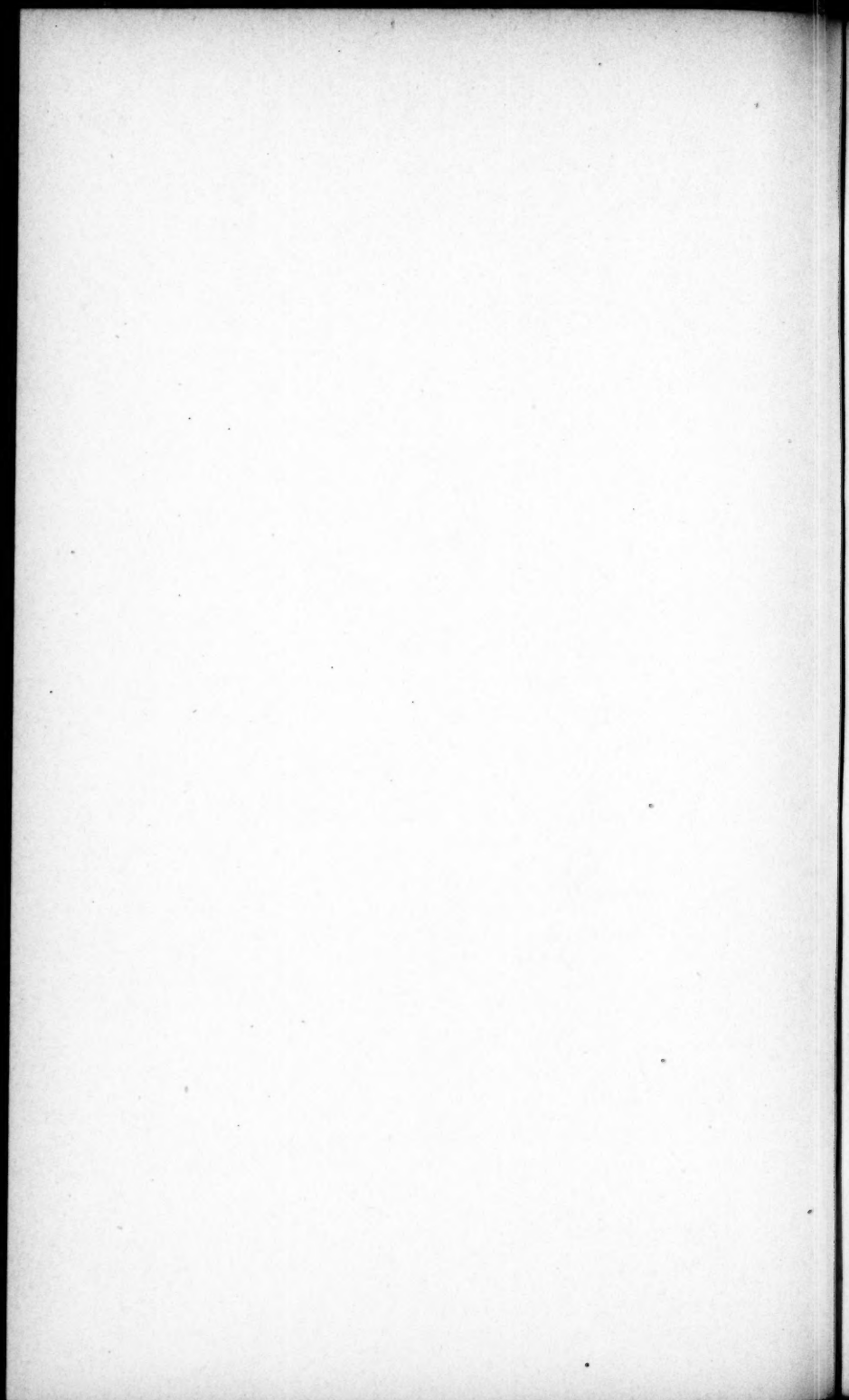
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

*A REVISION OF THE ATOMIC WEIGHT OF
NEODYMIUM.*

FIRST PAPER. — THE ANALYSIS OF NEODYMIUM CHLORIDE.

BY GREGORY PAUL BAXTER AND HAROLD CANNING CHAPIN.



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INTRODUCTION.

INVESTIGATIONS bearing upon the rare earths have always been particularly attractive on account of some unusual chemical and physical properties of these substances, their peculiar relations to the Periodic System, and in particular the important position which some of them have taken with relation to artificial illumination. To be sure any research involving the preparation of even one of the earths in a state of approximate purity is sure to be protracted, if not tedious. The very proof of the purity of a preparation is by no means easy to secure. The chief guides which have served in the determination of the purity of material have been the spectra, both absorption and emission, and the atomic weights. For a quantitative determination of purity the atomic weight is perhaps more frequently used than any other test. Hence for this reason as well as from theoretical considerations an exact knowledge of the atomic weights of the rare earths is very desirable.

The atomic weights of certain members of the group have received a singularly large amount of attention. Those of cerium and lanthanum, for instance, have been investigated more times than that of iron. Yet owing to the unusual difficulties in the preparation of pure material, as well as to troublesome analytical problems, the determinations of the atomic weights of the rare earths are probably of a lower order of accuracy than those of the common elements.

Among the standard methods which have heretofore been employed in the determination of atomic weights of the rare earths, the following are the most important:

The Analysis of the Oxalate. (Stolba.)¹ The dried oxalate is analyzed for the oxide by ignition, and for oxalic acid by titration with permanganate. The complete analysis of the salt is necessary on account of the invariable presence of an uncertain amount of crystal water even in the dried salt. Gibbs² has pointed out, on account of irregularity in the water content, the necessity of grinding thoroughly the whole specimen of oxalate which is to be used for analysis, in order to insure homogeneity of material. Furthermore it has been shown by Baxter and Griffin³ and Baxter and Daudt⁴ that the oxalate must be precipitated in acid solution, since in neutral or alkaline solution the oxalates of the alkalis and ammonium are carried down by the rare earth oxalate in considerable quantities. Brauner⁵ has found that in some cases at any rate the oxalate hydrolyzes in contact with water, although the magnitude of the latter error is doubtful. In spite of these difficulties the oxalate method is as easy to carry out as any and probably the most satisfactory for approximate purposes.

The Analysis of the Sulphate. The sulphates have been used for atomic weight purposes in several ways. Bahr and Bunsen⁶ first employed the method of dissolving weighed amounts of oxide in sulphuric acid, and weighing the sulphate after expelling the excess of acid. By the ignition of the oxalate it is doubtless possible to prepare the oxides in a very pure state if great care is taken to protect them from access to moisture or carbon dioxide, at any rate with elements which form trivalent compounds only. To prepare the sulphate in a neutral dry condition is a much more difficult proposition, owing to the retention of water and sulphuric acid if the temperature of heating is low, and

¹ Sitzungsber. böhm. Ges., Dec. (1878)

² Proc. Amer. Acad., 28, 261 (1893).

³ Jour. Amer. Chem. Soc., 28, 1684 (1906).

⁴ Ibid., 30, 563 (1908).

⁵ Trans. Chem. Soc., 81, 1266 (1902).

⁶ Lieb. Ann., 137, 5 (1866).

to decomposition with loss of sulphuric acid at higher temperatures. The investigations of Bailey,¹ Kruss,² Jones,³ Brauner,⁴ Wild,⁵ Brill,⁶ and Holmberg⁷ leave this matter still in a somewhat unsettled state.

The difficulty in obtaining the anhydrous sulphate in a neutral condition applies also to the method of ignition of sulphate to oxide. Furthermore it is probable that the oxide prepared by ignition from the sulphate retains traces of sulphuric acid.⁸

A third method depending upon the use of the sulphates involves the determination of the water in the octahydrated sulphate. Here the difficulty in obtaining crystals free from included cells of mother liquor is superimposed upon that of insuring complete dehydration.

The Analysis of the Chloride. The analysis of the chlorides has been little used on account of the tendency for the formation of insoluble basic compounds during drying. As Matignon⁹ has pointed out, if the dehydration of the chloride is conducted slowly and thoroughly enough in an atmosphere of dry hydrochloric acid gas, this difficulty disappears and a perfectly soluble product can be obtained, even after fusion. Hence on account of the accuracy with which halogen salts may be analyzed by precipitation with silver, this method is one of the best for atomic weight purposes. In testing the applicability of this method, we chose neodymium chloride for investigation, since neodymium compounds are comparatively easy to secure in an approximately pure state in large quantities. Furthermore, unlike its close relation praseodymium, neodymium does not readily change from the trivalent state.

Historical. The atomic weight of neodymium has already been determined many times, with discrepant results. This element and praseodymium, the other component of the old didymium, were first separated through the fractional crystallization of the double ammonium nitrates by Auer von Welsbach¹⁰ in 1885. He determined their atomic weights by Bunsen's method of converting oxide to sulphate, but apparently interchanged his results in publication, as first suggested by Brauner, as he gave the value 140.8 for neodymium and 143.6 for praseodymium.

¹ Trans. Chem. Soc., **51**, 683 (1887).

² Zeit. anorg. Chem., **3**, 46 (1893).

³ Amer. Chem. Jour., **28**, 31 (1902).

⁴ Trans. Chem. Soc., **81**, 1248 (1902).

⁵ Ibid., **38**, 195 (1904).

⁶ Ibid., **47**, 464 (1905).

⁷ Zeit. anorg. Chem., **53**, 124 (1907).

⁸ Brauner, loc. cit., 1263.

⁹ Compt. Rend., **133**, 289 (1901); **140**, 1182 (1905).

¹⁰ Sitzungsber. Akad. Wiss. Wien., **92**, 317 (1885).

In 1898 Brauner,¹ by converting oxide to sulphate, obtained the result 143.6 for neodymium. In this he included a correction for an impurity of 2.9 per cent of the corresponding praseodymium compound, estimated by comparison of the intensity of absorption spectra.

In the same year Boudouard² obtained a neodymium preparation by precipitation with potassium sulphate from some impure yttrium material. Apparently to identify the base rather than to establish its atomic weight, he analyzed the sulphate by converting it to oxide, with the result 143.0. Undoubtedly his material contained praseodymium, as no steps were taken to remove this inevitable impurity.

In 1898 Jones³ also investigated both neodymium and praseodymium with material purified by crystallization as the double ammonium nitrate. Cerium and lanthanum were eliminated by precipitation as basic nitrates, and a correction for residual praseodymium was obtained by comparing the intensities of its absorption bands in the neodymium preparations with those of the same bands in dilute praseodymium solutions of known strength. The atomic weight was found by converting the oxide to sulphate. The average of twelve results, ranging in value from 143.46 to 143.62, was 143.55. Corrected for praseodymium content this value becomes 143.60.

In 1901, after further purification of his original material, Brauner⁴ published another determination, which yielded the value 143.89. As this is the result of but one analysis and includes a correction of questionable accuracy for praseodymium impurity, it can hardly be given much weight.

Auer von Welsbach⁵ in 1903 published the results of further study of both neodymium and praseodymium. His source of material was a large quantity of double ammonium nitrates obtained as by-products in the technical extraction of lanthanum. A long series of fractional crystallizations as double ammonium nitrate served to free the neodymium from all but a trace of praseodymium. With this material, undoubtedly of very high purity, three analyses were made by the Bunsen method of converting oxide to sulphate, from which the atomic weight values 144.55, 144.52, and 144.57 respectively were obtained. Unfortunately no details of procedure are given.

A point of especial interest in connection with Jones's and Brauner's results is Auer's observation that the praseodymium absorption spectrum

¹ Proc. Chem. Soc., **14**, 70 (1898); Chem. News, **77**, 161 (1898).

² Compt. Rend., **126**, 900 (1898).

³ Amer. Chem. Jour., **20**, 345 (1898).

⁴ Proc. Chem. Soc., **17**, 66 (1901).

⁵ Sitzungsber. Akad. Wiss. Wien., **112**, 1037 (1903).

is weakened considerably by lanthanum and cerium ammonium nitrates and other salts, as well as by concentrated nitric acid, the effect of which was mentioned in Auer's earlier paper. Clearly any quantitative comparison of the intensity of the praseodymium spectrum from solutions of praseodymium salts alone, with that from solutions consisting mainly of other rare earth salts, is unreliable.

Feit and Przibylla¹ dissolved weighed amounts of various rare earth oxides in sulphuric acid and titrated the excess of acid, using methyl orange as the indicator. The endpoint was interfered with by the pink color of the neodymium salt, but this difficulty was obviated by comparing the solutions with standards containing the same amounts of indicator and neutral neodymium salt. Their neodymium material was prepared by fractional crystallization of the double magnesium nitrate. This preparation showed no trace of the strongest praseodymium and samarium absorption bands, although the "hellblau" color of the oxide was considered the best proof of its purity. Their result for the atomic weight of neodymium was 144.60.

Holmberg² after a study of the rare earth salts of twelve organic acids, selected the metanitrobenzol sulphonate as particularly suitable for the purification of neodymium, and by one hundred and sixty-two series of crystallizations obtained thirteen fractions ranging in atomic weight from 144.0 to 145.3. The purest fractions were selected and the oxide obtained by ignition of the oxalate was weighed and converted into sulphate. The value 144.10 was obtained as the mean of six results varying from 144.03 to 144.15.

The International Committee on Atomic Weights have chosen as the most probable value 144.3, which represents an average of the more recent determinations.

THE SEPARATION OF NEODYMIA FROM OTHER RARE EARTHS.

It is a well-known fact that when a salt of a mixture of rare earths is subjected to fractional crystallization, the less soluble salts tend to concentrate at the less soluble end of each series of fractions, and the more soluble salts at the opposite end of the series. In most cases it is less difficult to free an earth very thoroughly from more soluble impurities than it is to eliminate impurities which tend to concentrate in the crystals. An obvious although not generally recognized way out of the difficulty is to crystallize the substance in such different forms that impurities which tend to concentrate in the crystals in one case,

¹ Zeit. anorg. Chem., **43**, 202 (1905).

² Ibid., **53**, 83 (1907).

concentrate in the mother liquors in another, continuing the crystallization in any one form until impurities which accumulate in the mother liquors have been eliminated as completely as possible.

In the present instance the material was crystallized first as double ammonium nitrate from dilute nitric acid, then as nitrate from concentrated nitric acid. According to Auer von Welsbach,¹ in crystallization as double ammonium nitrates the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium- and yttrium-earths, while according to Demarçay,² in the crystallization of the nitrates from nitric acid the solubility first decreases with increasing atomic weight through gadolinium, 157.2, and then increases. In the crystallization as double ammonium nitrates samarium and the more soluble earths were eliminated, while in the crystallization of the nitrates from nitric acid the solubility of the first four of the above nitrates is reversed and the lanthanum, cerium and praseodymium were removed in the mother liquors.

Three and one half kilograms of neodymium ammonium nitrate, very kindly furnished by Dr. H. S. Miner of the Welsbach Light Company, served as a starting point in the preparation of pure material. The history of this material is somewhat uncertain, but, as nearly as can be determined, is as follows: Swedish cerite was decomposed with acid and the rare earths were precipitated as oxalates, from which the oxides were obtained by ignition. These oxides were then treated with nitric acid and the insoluble basic ceric salt was produced by heating. The lanthanum, praseodymium, neodymium, samarium, yttrium, etc., were obtained in solution. After the addition of ammonium nitrate the material had received, probably, about 150 to 250 crystallizations. Our treatment showed it to contain considerable lanthanum, cerium, and praseodymium, and a small amount of samarium. Probably traces of other rare earths were present, but no evidence of their existence was found even in the extreme fractions of the purified material.

In the further purification to which we subjected the double neodymium ammonium nitrate the usual method of fractional crystallization was followed: The whole material (1) was crystallized and the crystals (2) were separated from the mother liquor (3). The crystals were dissolved and again crystallized, the crystals becoming (4) and the mother liquor (5). The mother liquor (3) was evaporated to crystallization, and the crystals were combined with (5), while the mother liquor formed (6), and so on indefinitely. After the first few series of

¹ Sitzungsber. Akad. Wiss. Wien., **112**, 1043 (1903).

² Compt. Rend., **122**, 728 (1896); **130**, 1021 (1900).

crystallizations the number of fractions in each series was maintained nearly constant between twenty and twenty-five, and the different fractions were not allowed to vary much in size. As a rule the solutions were allowed to become supersaturated by cooling without crystallization, then they were seeded with tiny crystals of the purest neodymium salt available, and allowed to stand undisturbed over night in order that by the formation of large crystals the removal of mother liquor might be facilitated. On account of the extra labor and time involved, centrifugal drainage of the crystals is of little advantage where the composition of crystals and mother liquor differs as slightly as in the present case, and therefore was not employed. When the end fractions became small they were either temporarily removed and added to similar fractions subsequently obtained, or, if it could be plainly seen by the difference in color that they contained considerable impurity, they were rejected.

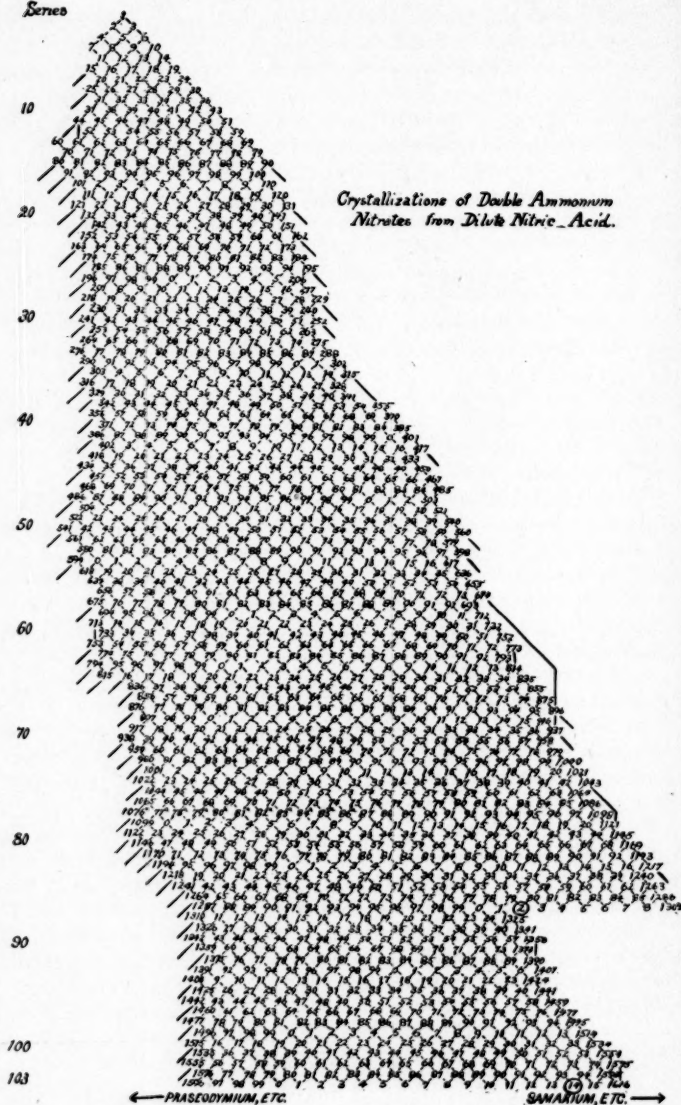
A diagram of the crystallizations as double nitrate is given on page 222. In any given series of crystallizations a lower number always indicates a less soluble fraction. A line not connecting an end fraction with any fraction in a subsequent series indicates rejection.

When eighty-six series of crystallizations had been completed, spectrograms were made of the absorption spectra of selected fractions in the last series, which contained fractions 1287 to 1309. These photographs were taken on Cramer's Trichromatic plates with a spectrograph employing glass lenses and prism and covered the range λ 650 — λ 380. The spectra indicated the presence of samarium in only a few of the more soluble fractions, 1306 to 1309. Praseodymium could be detected in all the fractions, although only traces were visible in the more soluble fractions.

In order to throw more light upon the progress of the purification approximate atomic weight determinations by the "permanganate" method¹ were carried out with portions of fractions 1290, 1299, 1303, and 1305. The oxalate was precipitated by adding a dilute solution of the double nitrate to a dilute solution of an excess of pure oxalic acid, and the precipitate was thoroughly washed, collected, and dried at 120°–130°. After very complete mixing of the highly crystalline material by grinding in an agate mortar, weighed portions of the oxalate were converted to oxide by ignition in platinum crucibles. Other portions, weighed out at the same time, were dissolved in dilute sulphuric acid and titrated with a standard solution of potassium permanganate. From the ratio $M_2O_3 : 3 C_2O_4$, the atomic weight was calculated.

¹ See page 216.

Series



Fraction.	Per cent of Nd_2O_3 .	Per cent of C_2O_4 .	Atomic Weight.
1290	0.5334	0.4193	143.9
	0.5334	0.4194	
	0.4195	0.4194	
	Average 0.5334	0.4194	
1299	0.5454	0.4274	144.3
	0.5452	0.4281	
	0.4278	0.4279	
	Average 0.5453	0.4278	
1303	0.5412	0.4258	143.8
	0.5412	0.4258	
	Average 0.5412	0.4258	
	0.5391	0.4217	144.6
	0.5390	0.4228	
	0.4218	0.4221	
	Average 0.5390	0.4221	
	0.5379	0.4212	144.6
	Average 0.5379	0.4212	
	Average of second and third values . .		144.6
1305	0.5447	0.4269	144.4
	0.5448	0.4272	
	0.4272	0.4269	
	Average 0.5448	0.4271	
	0.5414	0.4236	144.6
	0.4242	0.4239	
	Average 0.5414	0.4239	144.6
	Average		144.5

Fractions 1299 to 1305 were evidently very nearly identical and probably nearly pure, while fraction 1290 apparently contained about ten per cent of praseodymium, cerium and lanthanum.

At this point fraction 1302, which seemed on the whole to be the purest in this series, was set aside for more careful examination and analysis. Fractions 1303 to 1309 also, which contained the bulk of

the remaining samarium and yttrium earths, were separated from the others, and the fractionation was continued as before.

No further accumulation of samarium could be detected, after seventeen more series of crystallizations had been completed, in a spectrographic examination of the more soluble fractions of the one hundred and third series. Nevertheless the two most soluble fractions, 1615 and 1616, were rejected, and the next, 1614, was removed for subsequent analysis.

The sharpness with which the samarium is removed from the neodymium by the crystallization of the double ammonium nitrates is striking in comparison with the difficulty in eliminating the last traces of praseodymium in the same way. After the removal of only eight fractions, 1302 to 1309, the last of which was comparatively rich in samarium, seventeen series of crystallizations failed to reveal any residual samarium. On the other hand, when the fractions 1303 to 1309 were subjected to further fractional crystallization by themselves, the least soluble fraction of the fourteenth series was found to contain about one half per cent of praseodymium, estimated spectrographically as described later. By the same method fraction 1302, which contained more praseodymium than any one of the seven crystallized, was found to contain only 0.2 per cent of this impurity. Demarçay¹ and Feit and Przibylla² have emphasized the fact that neodymium and samarium may be separated with equal facility by crystallization as double magnesium nitrates.

At this point it seemed reasonably certain that practically all the more soluble rare earth impurities had been eliminated, while evidence of praseodymium could still be seen in the absorption spectra of all the fractions. For the removal of the praseodymium and at the same time cerium and lanthanum, if present, crystallization of the nitrates from concentrated nitric acid was next undertaken, since in this process these elements accumulate in the mother liquors.³

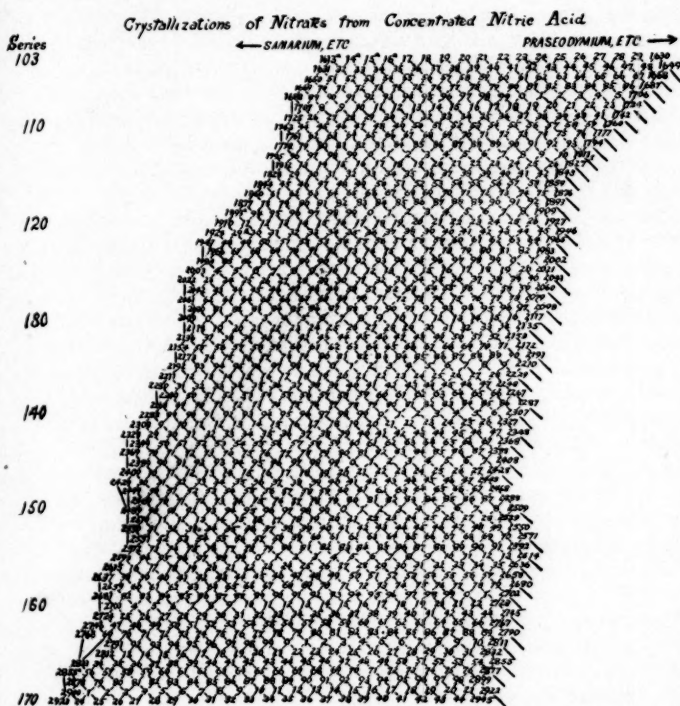
The ammonium nitrate was removed from the different fractions by evaporation and ignition, concentrated nitric acid was added, and the crystallization was carried through sixty-seven series. The same numbering was continued, except that the order of the one hundred and third series was reversed to give the less soluble fractions the lower numbers as before, 1613 becoming 1613a and 1596 becoming 1630. During these sixty-seven series no fractions were rejected at the less soluble end, although the extreme mother liquor was frequently re-

¹ *Compt. Rend.*, **130**, 1021 (1900).

² *Loc. cit.*, 207.

³ Demarçay, *loc. cit.*

jected. Thus any nitrate less soluble than neodymium nitrate would concentrate in the extreme crystal fraction of the last series. A diagram of this treatment follows:



The fractions of the last series, 2923 to 2945, were then converted to oxide by precipitation as oxalate from acid solution and ignition of the oxalate. The different fractions of oxide were all of the same lilac blue color. We could detect no difference in the color of the oxides of fractions found to be essentially free from praseodymium and those containing several tenths of a per cent of this impurity.

The final fractions were next subjected to careful comparative spectrographic examination, great pains being taken to have the conditions of experimentation the same for all the fractions. One gram of every

third fraction was dissolved in nitric acid, and, after the excess of acid had been evaporated, the solutions were diluted to the same volume, above five cubic centimeters. Photographs of the absorption spectra were made, the solutions being contained in test tubes of the same diameter, and various lengths of exposure being employed. The samarium band λ 401 was faintly visible in fraction 2923 only. This is not surprising, however, since, as has been stated before, no fractions had been removed from the less soluble end of the series in the course of all the sixty-seven series of crystallizations from concentrated nitric acid. Praseodymium could not be detected in fractions 2923 to 2932, but its strongest absorption band, λ 444, appeared with regularly increasing intensity in fractions 2935 to 2944.

In order to find out how much praseodymium can be detected in this way, and at the same time to estimate the proportion of praseodymium in the latter fractions, spectrograms were made, on one plate and with the same exposure, of the spectra of most of the solutions previously examined, and also of others similarly prepared from fractions 1302 and 1614, which had been removed at earlier stages of the fractionation. To a solution of fraction 2926, in which no praseodymium could be detected in the first photograph, 0.1 per cent of praseodymium oxide was added in solution, and the original concentration was restored by evaporation. The absorption spectrum of this specimen was photographed on the same plate as above, and again after the praseodymium content had been increased to 0.2, 0.5 and 1.0 per cent respectively. In the negative the first addition of 0.1 per cent made a distinct impression. From this it was concluded that fractions 2923 to 2932 contained less than that proportion of praseodymium. This assumption can scarcely be objected to on the ground that a considerable amount of praseodymium in fraction 2926 might have been brought within the limits of detection by means of a relatively small increment, because the intensity of the praseodymium band appeared to be proportional to the amounts of praseodymium added to the original solution.

Since these standards and the other solutions differed little except in praseodymium content, those giving praseodymium spectra of equal intensity could be safely assumed to contain the same percentage of this impurity. The results of the comparison of the different spectrograms are as follows:

Fraction	2935	2938	2941	2944	1302	1614
Per cent of Pr. . . .	0.05	0.1	0.2	0.5	0.2	0.15

Since a proportion of one tenth of a per cent of praseodymium lowers the atomic weight of neodymium by only four one thousandths of a

unit, the purer fractions were obviously as pure as it is worth while to make them. None of them in all probability were entirely free from praseodymium. In fact, visual spectroscopic examination of both fraction 2929 and 2931 with very strong absorption showed them to contain perceptible amounts of this impurity.

It is reasonable to suppose that cerium and lanthanum nitrates, which are more soluble in concentrated nitric acid than praseodymium nitrate, were removed from the neodymium even more completely than praseodymium. Evidence upon this point is more difficult to secure than in the case of praseodymium, on account of the lack of absorption bands of cerium and lanthanum in the visible spectrum. The following test for cerium was carried out with fraction 2944, which contained 0.5 per cent of praseodymium. The hydroxide was precipitated by the addition of an excess of sodium hydroxide, and, after washing by decantation, it was treated with saturated chlorine water for some time. A small quantity of undissolved hydroxide was filtered off and dissolved in nitric acid. To the nearly neutral solution a sufficient amount of a solution of calcium hypochlorite was added to produce a slight permanent precipitate. This precipitate was pink with no tinge of yellow. The same solution after the addition of a trace of cerium and testing with hypochlorite as before yielded a precipitate distinctly colored with the characteristic yellow of ceric hydroxide. Fraction 2944 was evidently nearly if not entirely free from cerium and the less soluble fractions of the series must have been purer still.

THE ABSORPTION SPECTRUM OF AQUEOUS SOLUTIONS OF NEODYMIUM SALTS.

The absorption spectra of two of the purest fractions, 2929 and 2931, were examined visually with a Hilger wave-length spectrocope. While no very great accuracy is claimed for the measurements, it is probable that the values are correct within one-millionth of a millimeter, for the spectrocope is capable of nearly ten times this accuracy for wave-lengths in the neighborhood of λ 500.

In the first two columns of the following table are given the values for the maxima of absorption observed during the gradual dilution of very concentrated, slightly acid solutions of the nitrates, each value having been obtained in the most dilute solutions in which the band could be observed. The spectra of the two fractions were identical.

The band λ 580 can be seen only at certain medium concentrations while the band λ 547 is visible only with very concentrated solutions. The praseodymium band λ 444 also was faintly visible only in the most

Baxter and Chapin Fractions 2929 and 2931. (1909).	Forsling and Holmberg. (1907).	Rech and Muthmann. (1906).	Auer von Welsbach. (1903).
			745 to 725
689	689.5		687
679	677.5	679.6	678
673	672.0	670.8	673
636	636.0	636.6	635
628	627.8	628.6	629
625	625.4	624.8	626
622	621.7	622.2	622
587		586.5	
583		583.2	583
580		580.8	
578	578.8 to 578.0	578.5	579
575	575.4	575.4	576
574	573.5	573.6	575
571	571.6	571.7	572.5
547			567.5
531	532.3	532.0	532
525		525.4	525
521	521.6	522.2	522.7
520	520.4	520.5	521
		514.5	
512	512.4	512.2	511.7
509	508.7	508.9	508.3
487	489.0 to 486.0	488.0	
480	479.9	479.8	
475	474.8 to 474.2	475.4	475.4
469	468.7	469.0	469.6
461	461.0	461.1	461
444 Pr		444.2	
		434.2	
433	433.0	432.9	432
		429.5	
		428.1	
427.5	427.1	427.2	426.5
418	418.3	418.2	417.8

concentrated solutions. The two bands λ 580 and λ 547 disappear if the nitrate is changed to chloride; otherwise the nitrate and chloride give maxima in essentially the same positions, although the relative intensities of the bands are somewhat different in the two cases.

The second, third, and fourth columns of the foregoing table represent the corresponding results obtained by Forsling from Holmberg's neodymium preparation,¹ by Rech from Muthmann's preparation,² and by Auer

¹ Zeit. anorg. Chem., **53**, 83 (1907).

² Zeit. Wiss. Photographie, Photophysik u. Photochemie, **3**, 411 (1906).

von Welsbach from his own material.¹ The last were taken from the drawings which were Auer's only published record, and since they are subject to two personal errors are less exact than the others. Being obtained, however, from very carefully prepared material, they should represent at any rate the number and the general location of the bands in the neodymium spectrum. Rech's measurements, since his material was less carefully prepared, include lines belonging to praseodymium and possibly to other elements.

While some of these bands are sharp, and appear in the same positions in solutions of various concentrations, others fade away gradually on the edges, and sometimes have their maxima shifted by changes in the concentration. Consequently the disagreement as to the exact positions of bands is due in many cases merely to differences in the conditions of observation. Furthermore, Forsling and Rech used chloride solutions, whereas Auer von Welsbach and the writers used nitrate solutions. On the whole the agreement between the different sets of values is very satisfactory. The bands between λ 587 and λ 571 are too close together to be distinguished from one another under any but the most favorable conditions. The double band λ 575 and λ 574 in particular separates only under rather limited conditions. The band at λ 579 in one of Auer's drawings may be intended to represent two lines at λ 580 and λ 577, and is thus interpreted by Kayser. Auer's band λ 567.5 appears very faintly in but one of his four drawings. There is a complete absence of shadow at this point in another drawing which represents a more concentrated solution, and which one would expect consequently to show the band. It is possible therefore that its appearance in the first print was merely accidental. The band λ 525 in concentrated solutions merges with λ 522 and in dilute it becomes invisible, so that it is not surprising that it was not observed by Forsling and Holmberg. The band λ 514.5, given by Rech alone, is coincident with no prominent band of any other rare earth, nor could it be detected in any of our preparations. The band λ 488 which both Forsling and Rech observed, as has already been stated, can be seen only with very strong absorption. This is doubtless the reason that it was not observed by Auer.

The presence or absence of the predominant impurities, praseodymium, cerium, lanthanum and samarium, in our best material has already been discussed. It is of some interest to consider other earths having prominent absorption bands in the visible spectrum.² Since none of

¹ Sitzungsber. Akad. Wiss. Wien., **112**, 1037 (1903).

² The following data are obtained from drawings by Urbain, Jour. de Chim. Phys., **4**, 31, 105, 232, 321 (1906).

these could have been present in quantity, their absorption bands obviously could be found only in concentrated solutions. The marked broadening and running together of the neodymium bands in concentrated solutions makes the detection of bands due to impurities difficult, except when these occur in regions in the spectrum comparatively free from neodymium bands. Of the three strong erbium bands λ 650, λ 540, and λ 522, the last two are completely masked by the neodymium in concentrated solution. The band λ 650, however, occurs in a region favorable for observation, and could not be detected even in the most concentrated solution. In the case of holmium the three strongest bands, λ 639, λ 535, and λ 485, all fall within the limits of neodymium bands at high concentrations. There was no evidence of the strongest, λ 535, in solutions of average concentrations. The strongest dysprosium band λ 451, which falls just within the broad neodymium band λ 484- λ 453, as it appeared in our most concentrated solutions, could not be detected. The terbium band λ 488 practically coincides with the neodymium band 487 which could be seen in our preparations only at the highest concentrations. Since this band could be seen of the same intensity in all our preparations, it is improbable that it represents an impurity of terbium. The sharp thulium band λ 700 does not fall within limits of any neodymium band, and we could find no evidence of its presence. Since the absorption of europium solutions in the visible spectrum is faint, and since all the stronger bands are masked completely by the bands of a concentrated neodymium solution, we have no spectroscopic evidence concerning the absence of this element. It may be added that, even in the extreme fractions of our crystal series, we could not detect the presence of any of these rarer elements. Further study of the absorption spectrum of neodymium is planned with the aid of a large quartz spectrograph, which has recently become available for us.

THE PREPARATION OF NEODYMIUM CHLORIDE.

The neodymium oxide fractions prepared as above were converted to chloride as follows: Fractions 1302 and 1614 were dissolved in the purest nitric acid in platinum vessels, the solutions were filtered, and the oxalate was precipitated from acid solution by means of the purest oxalic acid. After the oxalate had been washed by decantation and drained by suction upon a porcelain Gooch crucible employing a small disk of filter paper in place of an asbestos mat, the salt was dried and ignited in a platinum dish over a blast lamp. The oxide was dissolved in a quartz dish in hydrochloric acid which had been distilled with the use of a quartz condenser, and the chloride was three times

crystallized, with centrifugal drainage in platinum Gooch crucibles¹ in each case. The crystal yield was brought to a maximum by treating the solutions at 0° with hydrochloric acid gas obtained by warming concentrated solutions of the acid and led to the solutions through a quartz tube. Drying over sulphuric acid in a vacuum desiccator and powdering in an agate mortar completed the preparation for the final dehydration and analysis.

On account of the small quantity of material in each fraction of the final series, adjacent fractions were combined. The combinations actually analysed were 2923-2924, 2926-2927-2928, 2932-2933, and 2936-2937. A suspicion of contamination by platinum during the ignition of the oxides in platinum led to a slight change in the purification of these fractions. The original oxide was dissolved in hydrochloric acid in a quartz dish, and hydrogen sulphide, generated by the action of sulphuric acid on ferrous sulphide and thoroughly scrubbed with water, was passed into the hot, slightly acid solution. A slight black precipitate of platinum sulphide was formed in every case. The oxalate was precipitated from the filtered and boiled solution, and was collected and dried as before. In the ignition of this oxalate an electrically heated quartz muffle, kindly loaned to us by Dr. H. H. Willard, was used. Since the temperature of the muffle was very uniform, a lower temperature could be employed for the decomposition of the oxalate. The product of decomposition, which contained a large proportion of carbonate when obtained in this way, was dissolved in hydrochloric acid in a quartz dish and was crystallized as before. The first mother liquor, which in the case of fractions 1302 and 1614 had been slightly tinged with yellow, was in the case of all the other fractions free from such evidence of dissolved platinum.

THE PREPARATION OF PURE SILVER.

Pure silver was prepared by methods which have already been found to be very effective. Since these methods have been described in detail several times in papers from this laboratory,² only a brief outline of the processes is given here. Crude silver was dissolved in nitric acid, precipitated as chloride, reduced with alkaline invert sugar, and fused on charcoal. After cleansing by scrubbing with sand and etching with nitric acid, the buttons were again dissolved in nitric acid and the metal was precipitated from solution with ammonium formate. The

¹ Baxter, Jour. Amer. Chem. Soc., **30**, 286 (1908).

² See especially Richards and Wells, Pub. Car. Inst., No. **23**, 16 (1905); Jour. Amer. Chem. Soc., **27**, 472.

thoroughly washed product was fused with a blowpipe upon a crucible of the purest lime. Electrolytic deposition with silver nitrate as the electrolyte and with a dissolving anode of the pure silver buttons followed, and the electrolytic crystals were fused in a current of pure hydrogen on a boat of the purest lime. The resulting bars of metal were first cleansed with nitric acid and then were sawed into pieces of a convenient size with a fine jeweller's saw. After the fragments had been etched with nitric acid until free from surface contamination with iron from the saw, they were thoroughly washed with ammonia and pure water, and finally heated to about 300° C. in a vacuum. The silver was preserved in a desiccator over solid potassium hydroxide.

Pure silver nitrate was prepared by crystallization of the commercial product until free from chloride. That used in analyses 6, 7, 8, and 15 was a portion of material purified by Dr. Grinnell Jones for work upon the atomic weight of phosphorus.¹

In the preparation of reagents the precautions usual in exact work were taken. The ordinary distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone, through block tin condensers. Hydrochloric and nitric acids were distilled through quartz condensers, in the case of the hydrochloric acid the first and last runnings being rejected, in the case of the nitric acid two distillations being carried out, the first third being rejected in each distillation. By careful tests it was shown that nitric acid distilled in this way does not contain more than the merest trace of chlorine if the original acid is nearly free from the latter element.

Quartz or platinum utensils were employed wherever glass would have introduced objectionable impurities, and electrical heaters were used whenever the products of combustion of illuminating gas were to be avoided. In the crystallization of solids centrifugal drainage was always used to assist in the mechanical removal of mother liquor from crystals, except in the fractional crystallization of the neodymium material, where it would have been of little assistance.

THE DRYING OF THE NEODYMIUM CHLORIDE.

The drying of the neodymium chloride for analysis presented several difficulties. Matignon² states that if the chloride is first completely dehydrated and then fused in a current of dry hydrochloric acid gas, the product is completely soluble in water. Our earlier experiments

¹ Baxter and Jones, *Proc. Amer. Acad.*, **45**, 137 (1909); *Jour. Amer. Chem. Soc.*, **31**, 298.

² *Compt. Rend.*, **133**, 289 (1901).

did not confirm this statement, for in several instances salt which apparently had been very completely dried, after fusion in a current of hydrochloric acid gas was found to contain a considerable amount of basic salt. Since, however, material which had been dried at temperatures slightly below the melting point of the anhydrous salt gave absolutely clear solutions, the expedient was adopted of drying the salt for analysis as completely as possible without fusion, with the expectation of determining the water in subsequent experiments. During later experiments for determining the residual water it was found that the preliminary drying had not been effective in the earlier experiments, and that salt which has been dried as for analysis and then fused in a current of hydrochloric acid gas does give a perfectly clear solution. This information was unfortunately acquired too late to be of direct use in preparing the salt for analysis. Since, however, the dried but unfused salt was found to contain a constant very small proportion of moisture, and since a correction was applied for this moisture, no appreciable error could have been introduced by the incomplete drying. It is hoped, nevertheless, before long to institute further analyses with material which has been fused.

The apparatus employed in the drying of the neodymium chloride was essentially that used by numerous investigators in this laboratory for the dehydration of chlorides. Hydrochloric acid gas was generated by the action of concentrated sulphuric acid upon concentrated hydrochloric acid, and was dried by passage through five towers about thirty centimeters long and four centimeters in diameter filled with glass beads moistened with concentrated sulphuric acid. Nitrogen was prepared by Wanklyn's method of passing air through concentrated ammonia solution and then over hot copper. The excess of ammonia was removed and the nitrogen was purified and dried by passing over dilute sulphuric acid, silver nitrate solution, solid caustic potash, concentrated sulphuric acid, and resublimed phosphorus pentoxide. Nitrogen prepared in this way always contains hydrogen,¹ produced by the catalytic decomposition of the excess of ammonia in passing over the hot copper, in quantities which vary with the excess of ammonia, the temperature of the copper, as well as the length of the copper layer and the speed of the gases. The hydrogen could not have had any effect upon the neodymium chloride, however, and is an advantage in preventing the attacking of the platinum boat. Air was purified and dried by reagents similar to those used in the purification of the nitrogen. The hydrochloric acid apparatus was constructed wholly of glass,

¹ Our attention was first called to this fact by Dr. R. C. Wells.

and the nitrogen and air purifying trains had short rubber connections only at the beginning. Any one of these gases or any desired mixture could be delivered through the tube in which the boat containing the salt was placed. This tube could be heated to constant temperatures in an oven consisting of two superimposed solid aluminum blocks.¹

According to Matignon,² at about 105° C. neodymium chloride loses five of its six molecules of water of crystallization rapidly, while the sixth molecule appears at 160°. We have determined the melting point of the hexahydrated chloride (made from fraction 2931) to be 124°. Thus the drying of the chloride may be caused to take place by a process of double efflorescence, a condition very favorable for the complete elimination of the water. Richards³ has pointed out that a hydrated salt dried wholly by efflorescence can be freed from moisture much more effectively than one which has been allowed to melt during the dehydration, hence care was taken to keep the temperature below 124° until the greater part of the water had been expelled.

The powdered crystals of neodymium chloride were placed in a platinum boat which had been previously weighed in a weighing bottle, and the boat was heated in a current of mixed nitrogen and hydrochloric acid gases at gradually increasing temperatures. The boat was contained in a hard glass tube which formed part of a "bottling apparatus,"⁴ and this in turn was attached to the systems for purifying the various gases. The temperature was kept below 124° until the larger portion of the water had been expelled. Then it was gradually raised to 200°, and finally the salt was heated at about 330° for one hour in a current of pure hydrochloric acid gas. During the heating there was never the slightest appearance of melting. In the first five analyses the final temperature was higher than in the subsequent ones, and was not far below the fusing point of the anhydrous salt. After the tube had been allowed to cool, the hydrochloric acid was displaced by nitrogen and finally by air, and the boat was transferred to the weighing bottle without exposure to moist air by means of the bottling apparatus. After long standing in a desiccator near the balance the boat and contents were weighed.

¹ Baxter and Coffin, *Proc. Amer. Acad.*, **44**, 184 (1909); *Jour. Amer. Chem. Soc.*, **31**, 206.

² *Compt. Rend.*, **133**, 289 (1901).

³ *Zeit. physik. Chem.*, **46**, 194 (1903).

⁴ Richards and Parker, *Proc. Amer. Acad.*, **32**, 59 (1896).

THE METHOD OF ANALYSIS.

In order to dissolve the chloride the boat was first transferred to a large dry Erlenmeyer flask, a column of bulbs was inserted in the neck of the flask and enough water to cover the boat was introduced through the bulbs. These precautions were taken because of the violence of the action of the water upon the finely divided anhydrous salt, in order to avoid both mechanical loss of material and possible evaporation of hydrochloric acid owing to hydrolysis at the high temperature which results at the moment when the salt comes in contact with water. That this error is not a serious one is evident from the fact that although in the first five analyses the use of the column of bulbs was omitted, yet the results of these analyses are not markedly different from the others. The solution was allowed to stand in the flask for some time in order to ensure absorption of any volatilized hydrochloric acid. Every specimen of salt dried and dissolved in this way gave a perfectly clear solution.

The solution of the neodymium chloride was diluted to a volume of about one liter with water containing a small amount of nitric acid. Then an equally dilute solution of a very nearly equivalent amount of pure silver nitrate containing nitric acid was added to the solution of the chloride. The glass-stoppered precipitating flask containing the solution was thoroughly shaken and allowed to stand for about twenty-four hours, and then an excess of silver nitrate of about one tenth of a gram was added to complete the precipitation.

After standing until the supernatant liquid was perfectly clear, the precipitate was thoroughly washed, first with dilute silver nitrate solution and then with very dilute nitric acid in the earlier analyses, with pure water in the later ones, and was collected upon a weighed Gooch-Munroe-Neubauer crucible. Then, after the crucible and contents had been dried in an electric air bath at about 150° for eighteen hours, they were weighed.

The moisture retained by the dried silver chloride was estimated in each analysis by determining the loss in weight during the fusion of the dried silver chloride in a weighed porcelain crucible. The weight of silver chloride dissolved in the filtrate and silver nitrate wash-waters was assumed to be 0.00003 gram per liter.¹ That dissolved in the acid or aqueous washings together with the ammonia rinsings of the precipitating flask was determined by comparison with standard solutions in

¹ Richards and Wells, Pub. Car. Inst., No. 28, 30 (1905); Jour. Amer. Chem. Soc., 27, 487.

a nephelometer, the usual precautions being taken to secure uniformity of precipitation.¹

When the ratio of the neodymium chloride to metallic silver was to be determined a quantity of silver equivalent to the chloride within a very few tenths of a milligram was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. The quantity of silver was adjusted exactly by means of a hundredth normal solution of silver. After the silver solution had been freed from oxides of nitrogen it was diluted to a volume of one liter and was quantitatively added to the chloride solution. The precipitate was caused to settle completely by occasional shaking and standing for several days. Then portions of the mother liquor were tested for excess of silver or chloride by the addition of hundredth normal chloride or silver nitrate solutions, and comparison of the opalescence produced in a nephelometer. Deficiencies in either chloride or silver were made up by means of the dilute standard solutions of these substances until finally exactly equivalent amounts of chloride and silver were present in the solution.

In all except the first two titrations the solubility of the silver chloride in the mother liquor was very much decreased by cooling the solution with ice water, a method of increasing the accuracy of nephelometric observation which has been devised recently by Richards and Willard and used successfully in their revision of the atomic weight of lithium.²

As soon as equilibrium had been reached in a titration, an excess of one tenth of a gram of silver nitrate was added and the silver chloride was determined gravimetrically as described above. Corrections were of course applied for any chloride added in the titration.

THE DETERMINATION OF THE MOISTURE RETAINED BY THE NEODYMIUM CHLORIDE.

Although in several cases where hydrated salts have been dried by efflorescence it has been shown that the moisture retained by the salt is negligible in quantity,³ in the present instance careful experiments were instituted to test this point thoroughly. The direct determination of the water by absorption with phosphorus pentoxide, after fusion of the salt, was complicated in the case of neodymium chloride, since,

¹ Richards and Wells, *Amer. Chem. Jour.*, **31**, 235 (1904); **35**, 510 (1906). Richards and Stähler, *Pub. Car. Inst.*, No. **69**, 20 (1907); *Jour. Amer. Chem. Soc.*, **29**, 635.

² *Pub. Car. Inst.*, No. **125**, 30 (1910); *Jour. Amer. Chem. Soc.*, **32**, 32.

³ Baxter and Coffin, *Jour. Amer. Chem. Soc.*, **28**, 1587 (1906); Baxter and Tilley, *Ibid.*, **31**, 212 (1901).

if the salt is fused in nitrogen, after being dried, hydrochloric acid is liberated owing to hydrolysis with the residual moisture. Fusion in a current of hydrochloric acid gas is not permissible because of the action of this gas upon the phosphorus pentoxide¹ necessary for the absorption of the water.

Fortunately neodymium chloride is only very slightly volatile at temperatures not far above its fusing point,² so that it is possible to estimate the moisture content of the dried salt by fusion in a current of hydrochloric acid gas and determination of the loss in weight. The trace of chloride volatilized during the fusion can then be collected and weighed.

For these experiments a glass tube is obviously unsuited owing to the action of the hydrochloric acid upon the glass at the fusing point of the chloride and consequent vaporization of alkali chloride into the neodymium chloride as well as into the cooler parts of the tube. Hence in these experiments a quartz tube was substituted for glass. This tube was apparently not attacked by the hydrochloric acid gas during a long series of experiments.

The exact procedure was as follows: The boat with a maximum charge of neodymium chloride crystals was heated in a current of nitrogen and hydrochloric acid gases, and was bottled and weighed exactly as in preparing the salt for the chloride analyses. After being weighed the boat was replaced in the quartz tube, and when the air had been completely displaced by hydrochloric acid gas, the tube was electrically heated by means of a removable mica sleeve wound with the resistance wire "Nichrome," until the salt was fused. The boat was then bottled in dry air a second time and reweighed. In nearly every experiment a barely visible condensation of concentrated hydrochloric acid solution took place in the cool portion beyond the boat.

Weight of NdCl ₃ .	Loss in Weight during Fusion.	Percentage Loss in Weight.
gm.	gm.	
5.36	0.00045	0.0084
6.73	0.00052	0.0077
5.93	0.00050	0.0084
Average		0.0082

¹ Baxter and Hines, Jour. Amer. Chem. Soc., **28**, 779 (1906).

² Neodymium chloride fuses at 785° and is not volatile at 1000° according to Matignon. Compt. Rend., **133**, 289 (1901); **140**, 1340 (1905).

The loss in weight of the salt found in this way is caused in part by a slight sublimation during the fusion, the magnitude of which was not determined in the first series of experiments. Since the neodymium chloride employed in the moisture determinations was not of so high grade of purity as that used in the chloride analyses, the volatilized material probably consisted in part of other chlorides. Hence the proportion of moisture calculated from the loss in weight is certainly a maximum. In a second series of experiments, after the fusion of the salt, the sublimate in the quartz tube was dissolved in water and the solution was evaporated to dryness in the weighed platinum boat, and after drying at 135° in hydrochloric acid gas the boat was reweighed.¹ The weights thus obtained were subtracted from the loss in weight of the salt found in the same experiment. When the quartz tube was heated alone in hydrochloric acid gas, no sublimate was formed, showing that the volatilized substance did not come from the quartz.

Weight of NdCl ₃ .	Loss in Weight during Fusion.	Weight of Volatile Matter.	Per cent of Moisture.
gm. 6.24	gm. 0.00050	gm. 0.00030	0.0032
7.19	0.00052	0.00030	0.0031
Average			0.0032

It is to be noted that the percentage loss in weight in the second series of experiments is identical with that of the first series, although the per cent of moisture is less than half the percentage loss in weight during fusion. The effect upon the atomic weight of neodymium of correcting for the moisture is to lower the atomic weight by eight thousandths of a unit.

The percentage of moisture found is nearly identical in magnitude with that obtained from iodine pentoxide which had been made by efflorescence of iodic acid, 0.0023.²

The fused neodymium chloride seemed to be perfectly soluble in water, the probable reason for the better success in these experiments than in the earlier ones being the more efficient drying of the salt before fusion.

¹ The moisture retained by neodymium chloride at this temperature is only 7.5 per cent of its weight. A higher temperature was avoided in order that no portion of the residue might volatilize.

² Baxter and Tilley, Jour. Amer. Chem. Soc., **31**, 212 (1909).

THE SPECIFIC GRAVITY OF NEODYMIUM CHLORIDE.

Although Matignon¹ had already found the density of anhydrous fused neodymium chloride at 18° referred to water at 4° to be 4.195, for the purpose of confirmation this constant was redetermined by displacement of toluol. On account of the difficulty of removing air from porous material the salt was fused for these determinations instead of being dried. The pycnometer employed was one of special form, modified by Baxter and Hines.²

The salt was first carefully dried and then finally fused in a current of hydrochloric acid gas in a small platinum boat, as previously described. The boat and contents were then weighed in a small weighing bottle to which they were transferred by means of the bottling apparatus. The salt was next quickly covered with dry toluol and a special pycnometer stopper was substituted for the ordinary stopper of the weighing bottle. Entangled air was removed by exhaustion in a desiccator and finally the toluol was adjusted to a mark in a capillary outlet tube in the usual way, after the temperature of the system had been carefully adjusted to 25°. In order to avoid evaporation of the toluol through the ground joint of the pycnometer this was made tight by means of a weighed quantity of syrupy phosphoric acid. The toluol content of the system being known, the displaced toluol could be found. The specific gravity of the toluol at 25° referred to water at 4° was determined in the same pycnometer to be 0.8636, while Jones³ in earlier experiments with a different pycnometer found the specific gravity of the same sample to be 0.8633.

Weight of NdCl ₃ in Vacuum.	Weight of Toluol dis- placed in Vacuum.	Specific Gravity of NdCl ₃ . 25°/4°.
gm.	gm.	
1.9967	0.4177	4.128
3.6878	0.7700	4.136
3.2569	0.6798	4.137
Average		4.134

A part of the difference between this value and Matignon's can be explained by the different temperatures at which the determinations were made.

¹ Compt. Rend., **140**, 1340 (1905).

² Amer. Chem. Jour., **31**, 222 (1904).

³ Baxter and Jones, Proc. Amer. Acad., **45**, 155 (1910); Jour. Amer. Chem. Soc., **31**, 314.

If the weights are assumed to have the specific gravity at 8.3,¹ Matignon's value for the density leads to a vacuum correction per gram of substance of +0.000141, while the value 4.13 necessitates a correction of +0.000145. The difference amounts to only four ten thousandths of a percent, which corresponds to a difference of only one thousandth of a unit in the atomic weight of neodymium. Hence it is of no importance which correction is employed.

The following table indicates the corrections for the buoyant effect of the air applied to the weights of the various substances.

	Specific Gravity.	Vacuum Correction.
Weights	8.3	
Toluol	0.863	+0.00126
NdCl ₃	4.134	+0.000145
AgCl	5.56	+0.000071
Ag	10.49	-0.000031

All weighings were made on a nearly new balance, Troemner No. 10, which is employed exclusively in atomic weight researches. Weighings were made by substitution for counterpoises as nearly as possible like the objects weighed both in weight and in volume. The weights were carefully standardized to hundredths of a milligram by the method described by Richards.²

RESULTS AND DISCUSSION.

In order to show that no appreciable error occurred owing either to occlusion by silver chloride or from loss of silver chloride in solution, the ratio between the silver used and the silver chloride obtained has been calculated in the five pairs of analyses for which the data are available.

Analyses.	Ag: AgCl.
8 and 16	0.752663
10 and 17	0.752726
12 and 19	0.752626
13 and 20	0.752686
14 and 21	0.752621
Average	0.752664

¹ Baxter, Proc. Amer. Acad., **42**, 209 (1906).

² Jour. Amer. Chem. Soc., **22**, 144 (1900).

ATOMIC WEIGHT OF NEODYMIUM.

SERIES I. $\text{NdCl}_3 : 3 \text{AgCl}$. $\text{Cl} = 35.457$. $\text{Ag} = 107.880$

No. of Analysis.	Fraction.	Corrected Weight of NdCl_3 in Vacuum.	Weight of AgCl in Vacuum.	Loss on Fusion.	AgCl Dissolved in Wash Water.	AgCl added in Titration.	Corrected Weight of AgCl in Vacuum.	Ratio $\text{NdCl}_3 : 3 \text{AgCl}$.	Atomic Weight of Neodymium.
1	1302	3.16218	5.42334	0.00030	0.00242	gm.	gm.	0.582841	144.257
2	1302	2.93305	5.02969	0.00047	0.00304		5.42546	0.582850	144.262
3	1302	2.99149	5.12978	0.00019	0.00236		5.03226	0.582915	144.289
4	1302	2.62468	4.50114	0.00030	0.00254		5.13195	0.582825	144.250
5	1614	2.38439	4.08848	0.00025	0.00241		4.50338	0.582858	144.265
6	1614	2.55827	4.38789	0.00029	0.00131		Average	0.582889	144.278
7	1614	3.59114	6.15981	0.00026	0.00140		4.09064	0.582894	144.280
8	2923-4	4.27402	7.33208	0.00023	0.00218	0.00200	4.38891	0.582887	144.277
9	2926-7-8	4.69459	8.06313	0.00029	0.00160		6.16095	0.582890	144.278
10	2926-7-8	2.79574	4.80313	0.00025	0.00142	0.00800	Average	0.582925	144.293
11	2932-3	2.59810	4.45553	0.00039	0.00227		7.33203	0.582857	144.264
12	2932-3	3.42064	5.87107	0.00021	0.00196		8.05444	0.582895	144.280
13	2932-3	4.11855	7.06994	0.00018	0.00172	0.00410	4.79630	0.582876	144.272
14	2936-7	3.95958	6.79583	0.00017	0.00179	0.00630	Average	0.582872	144.270
15	2936-7	2.71834	4.66295	0.00011	0.00111	0.00400	5.86872	0.582860	144.265
General Average									144.298
									144.278
									144.262
									144.257
									144.260
General Average									0.582876
									144.272

ATOMIC WEIGHT OF NEODYMIUM.

SERIES II. $\text{NdCl}_3 : 3 \text{ Ag}$. $\text{Ag} = 107.880$. $\text{Cl} = 35.457$.

Number of Analysis.	Fraction.	Corrected Weight of NdCl_3 in Vacuum.	Weight of Ag in Vacuum.	Weight of Ag added.	Corrected Weight of Ag in Vacuum.	Ratio $\text{NdCl}_3 : 3 \text{ Ag}$.	Atomic Weight of Neodymium.
16	2923-4	4.27402	5.51825	0.00030	5.51855	0.774482	144.283
17	2926-7-8	2.79574	3.60989	0.00041	3.61030	0.774379	144.249
18	2932-3	2.77391	3.58159	0.00037	3.58196	0.774411	144.259
19	2932-3	3.42064	4.41676	0.00019	4.41695	0.774435	144.267
20	2932-3	4.11855	5.31786	0.00000	5.31786	0.774475	144.280
21	2936-7	3.95958	5.11284	0.00050	Average	0.774440	144.269
22	2936-7	4.04435	5.99649	0.00041	5.11289	0.774431	144.266
					5.99699	0.774447	144.271
					Average	0.774439	144.269
General Average							144.268
Average of all the Results in Series I and II							144.270

RESULTS AVERAGED BY FRACTIONS.

Fraction.	1302.	1614.	2923-4.	2926-7-8.	2932-3.	2936-7.	Average.
$\text{NdCl}_3 : 3 \text{ AgCl}$							144.274
$\text{NdCl}_3 : 3 \text{ Ag}$	144.265	144.278	144.293	144.272	144.278	144.260	144.268
Average of all Individual Analyses	144.265	144.278	144.288	144.264	144.273	144.264	144.272
Corrected for Praseodymium	144.273	144.284	144.288	144.264	144.273	144.268	144.275

The average ratio of silver to silver chloride is within four thousandths of a per cent of that obtained by Richards and Wells,¹ 0.752634 : 1.000000.

The results in the preceding tables add further evidence to that already obtained by the spectroscope, that all the samples analyzed were of a high degree of purity. Fraction 2923-4 contained all the rare earth impurities of higher atomic weight than neodymium which accumulated in sixty-seven series of crystallizations, and actually was found to contain a trace of samarium, while fraction 2936-7 contained more praseodymium, probably not more than 0.1 per cent, than any other fraction of the last series which was analyzed. The first impurity raises the atomic weight and the second lowers it; yet the difference in the average results of these two extreme fractions is only 0.024. The fractions 1302 and 1614 gave results differing from those of fractions known to be slightly purer by amounts no larger than the experimental error. When corrected for the proportion of the chief impurity, praseodymium, the results agree satisfactorily for all the samples except fraction 2923-4, which certainly contained an unestimated proportion of samarium.

The results obtained from fractions 1302, 1614, and 2923-4 naturally are less reliable than those obtained from the other three fractions. The corrected average for fractions 2926-7-8, 2932-3, 2936-7, is, however, 144.268, which differs from the corrected average for all six fractions, 144.275, by less than 0.01. It is evident that the value 144.27 can safely be taken to represent with accuracy the atomic weight of the purest material which we have succeeded in preparing. This value is essentially identical with the one chosen by the International Committee upon Atomic Weights, 144.3, and lies midway between the results of Auer von Welsbach and Feit and Przibylla on the one hand and that of Holmberg on the other.

We are indebted particularly to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels, as well as to the Welsbach Light Company for the neodymium material.

SUMMARY.

1. It is emphasized that crystallization in more than one form is advisable for the preparation in a pure state of salts of rare earths.
2. The preparation of a very pure neodymium salt is described.

¹ Pub. Car. Inst., No. 28, (1905); Jour. Amer. Chem. Soc., 28, 456.

3. The absorption spectrum of neodymium is described.
4. A method of obtaining anhydrous neodymium chloride is given.
5. The specific gravity of anhydrous neodymium chloride is found to be 4.134 at $25^{\circ}/4^{\circ}$.
6. The most probable value of the atomic weight of neodymium is found to be 144.27, if silver is taken at 107.88; with silver at 107.87 neodymium becomes 144.26.

